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Electronic supplementary information

For

B-H and O-H bonds activation via a single electron transfer of frustrated radical pairs

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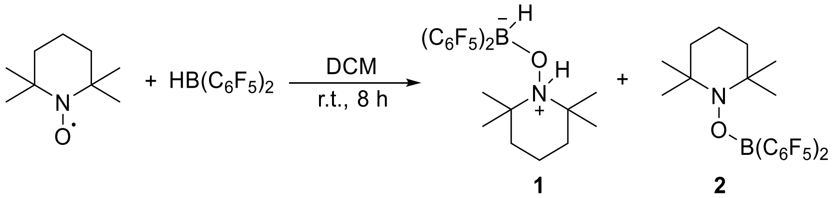
General information

X-Ray diffraction: Single-crystal X-ray diffraction data were collected on a Bruker Smart APEX II CCD single-crystal diffractometer (compounds 1, 6 and 7) or a Bruker D8 Venture CMOS-based diffractometer (compounds 5, 8 and 9) with graphite-monochromated Mo_{Ka} radiation (λ = 0.71073 Å). All of the data were corrected for absorption effects using the multi-scan technique. Final unit cell parameters were based on all observed reflections from integration of all frame data. The structures were solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization that implanted in Olex2. For all compounds, all non-H atoms were refined anisotropically unless otherwise stated, and hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. CCDC-2064567 (1), CCDC-2064569 (5), CCDC-2064565 (6), CCDC-2064566 (7), CCDC-2064570 (8) and CCDC-2064568 (9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/. *Exceptions and special features*: For compound 1, restraint(FIX) was used in order to fix the Uiso value of H2 to a reasonable value. For compound 6, H2 was modeled and refined isotropically at two positions. For compound 8, the solvent mask was used to remove a badly disordered dichloromethane molecule. The final reported sum formula is included the solvent molecule.

NMR spectra and crystallographic data of compound 1



Scheme S1

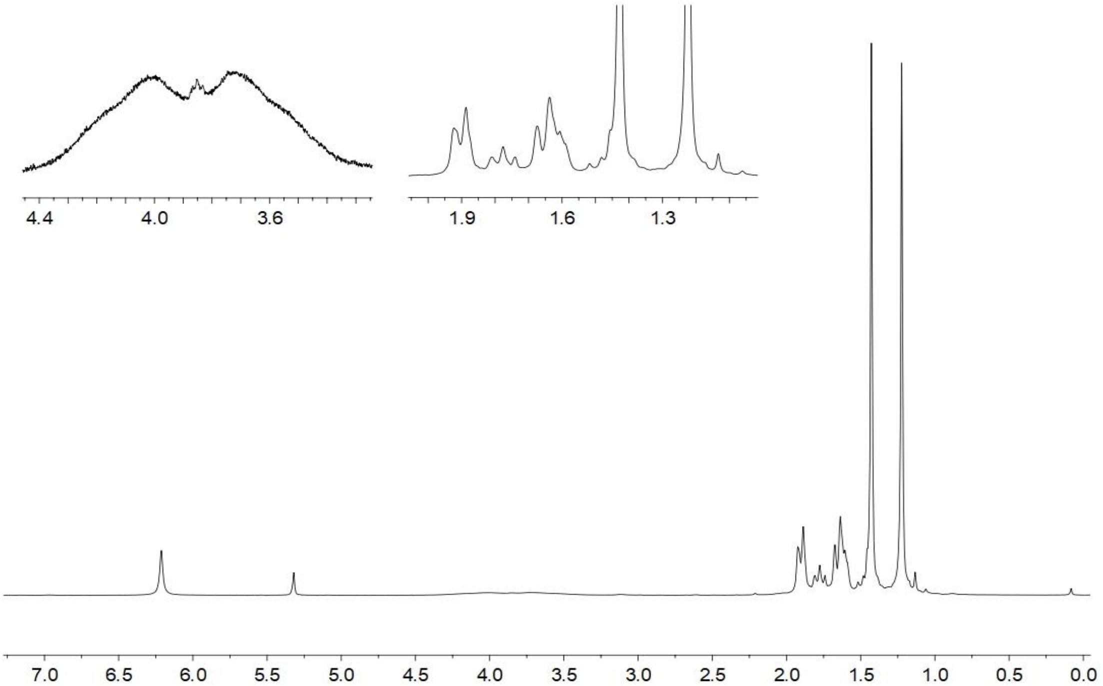


Fig. S1 ^{1}H NMR (400 MHz, 299 K, CD_2Cl_2) spectrum of compound **1**.

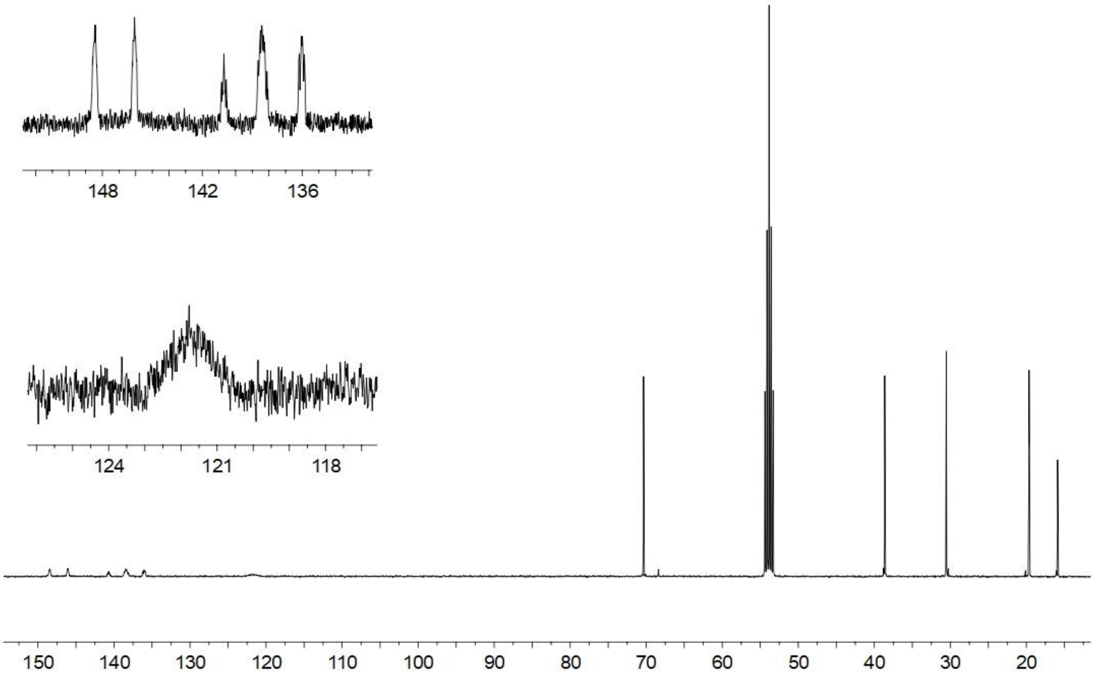


Fig. S2 $^{13}C\{^1H\}$ NMR (101 MHz, 299 K, CD_2Cl_2) spectrum of compound **1**.

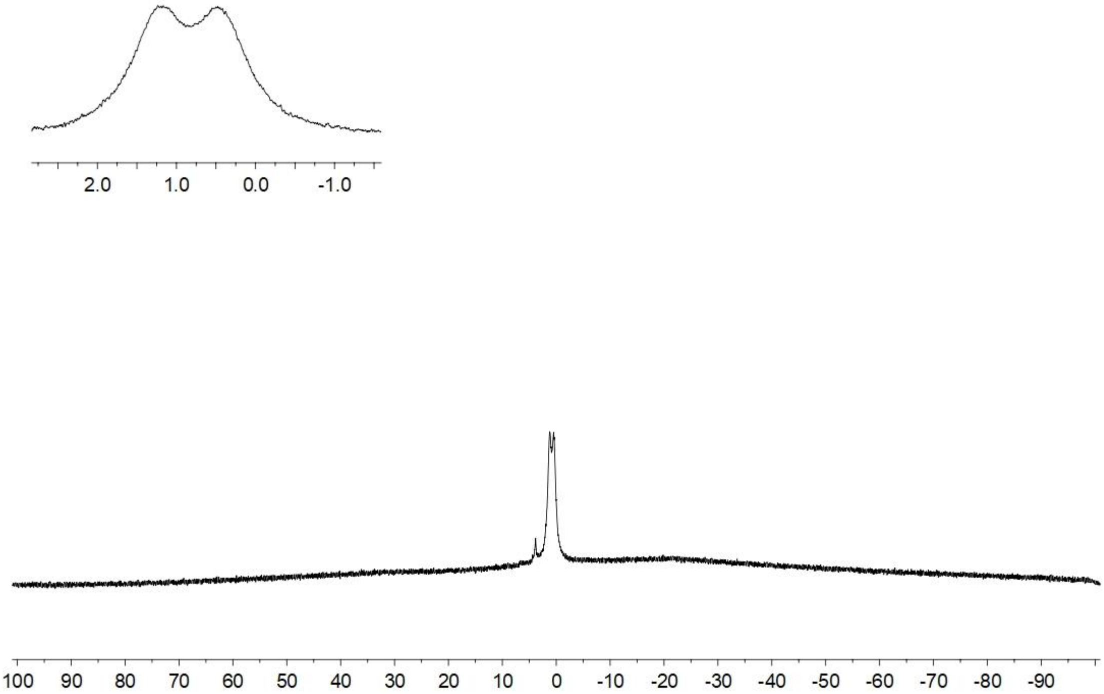


Fig. S3 ^{11}B NMR (128 MHz, 299 K, CD_2Cl_2) spectrum of compound **1**.

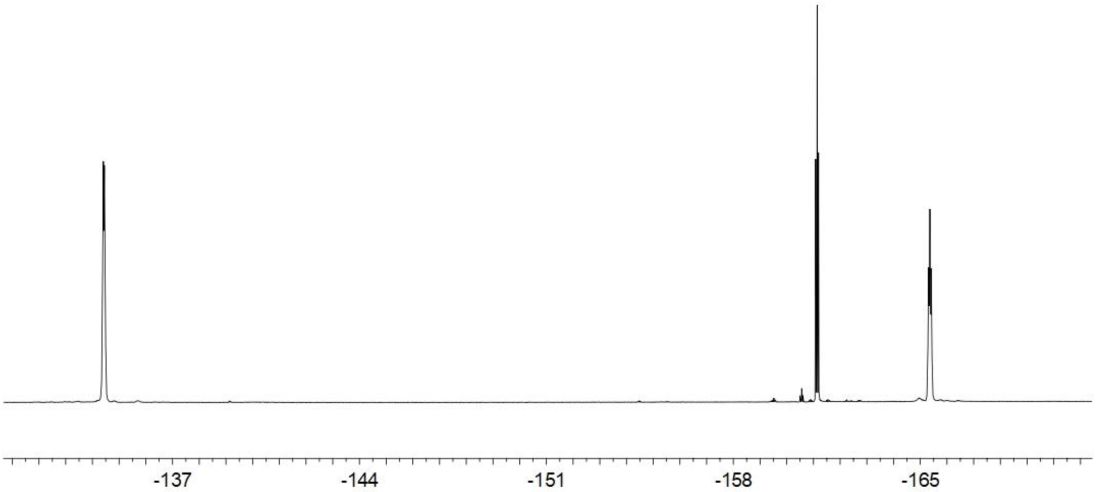


Fig. S4 $^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2) spectrum of compound **1**.

X-ray crystal structure analysis of compound 1: formula $C_{27}H_{20}BD_6F_{10}NO$, M = 587.33, colorless crystal, 0.35 x 0.2 x 0.2 mm, a = 11.24090(10), b = 11.76880 (10), c = 12.12320(10) Å, α = 63.9275(5), β = 81.7456(5), γ = 65.3098(5)°, V = 1307.32(2) Å^3, ρ_{calc} = 1.492 gcm^{-3}, μ = 0.138 mm^{-1}, empirical absorption correction ($0.6599 \leq T \leq 0.7461$), Z = 2, triclinic, space group P-1 (No. 2), λ = 0.71073 Å, T = 173 K, ω and φ scans, 20796 reflections collected (±h, ±k, ±l), 5987 independent (R_{int} = 0.0165) and 5243 observed reflections [$I>2\sigma(I)$], 455 refined parameters, R = 0.0392, wR^2 = 0.0961, max. (min.) residual electron density 0.378 (-0.244) e.Å^{-3}, the positions of the hydrogen atom at N1 and B1 were refined freely; others hydrogen atoms were calculated and refined as riding atoms.

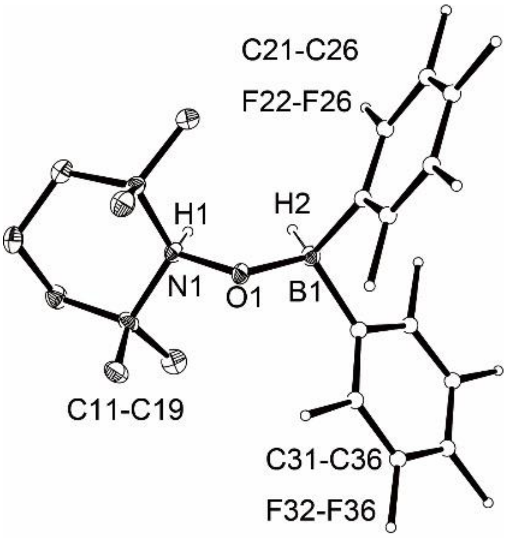


Fig. S5 Molecular structure of compound **1** (thermal ellipsoids are shown at the 50% probability level). Hydrogen atoms except for N1–H1 and B1–H2 are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-O1 1.414(1), B1-O1 1.520(2); B1-O1-N1 114.77(9), $\sum N1^{CCO}$ 338.61, $\sum B1^{CCO}$ 328.38.

NMR spectra of compound 2:

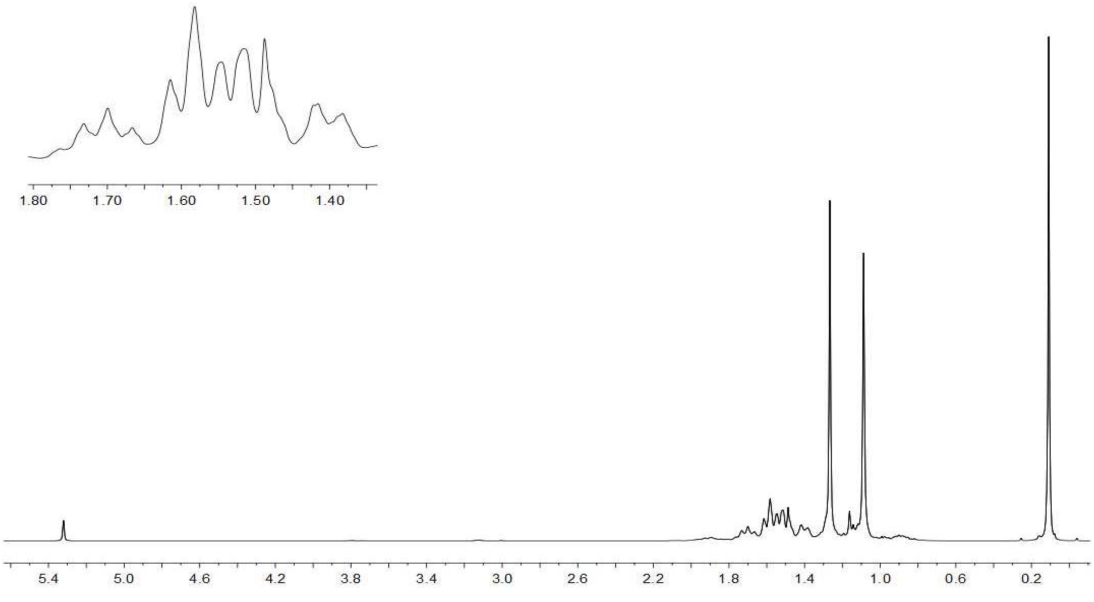


Fig. S6 ^{1}H NMR (400 MHz, 299 K, CD_2Cl_2) spectrum of compound **2**.

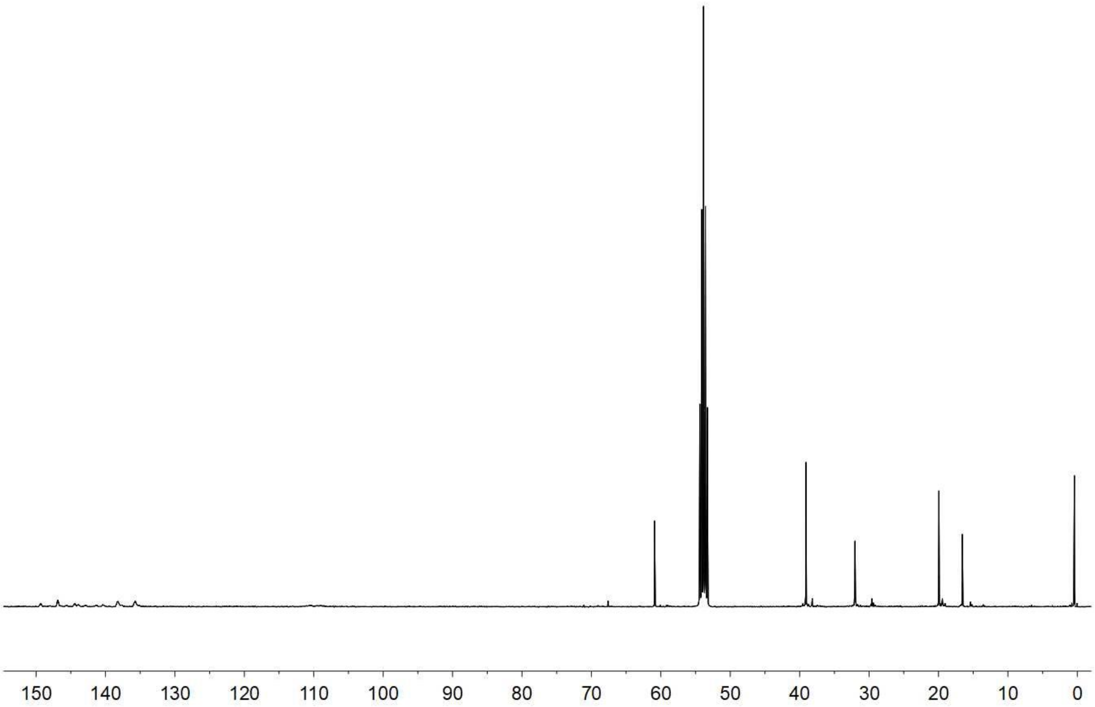


Fig. S7 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299 K, CD_2Cl_2) spectrum of compound **2**.

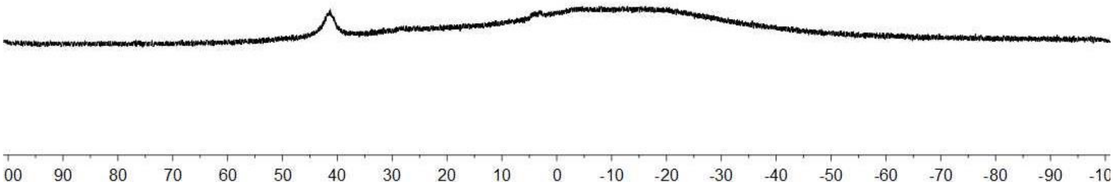


Fig. S8 ^{11}B NMR (128 MHz, 299 K, CD_2Cl_2) spectrum of compound **2**.

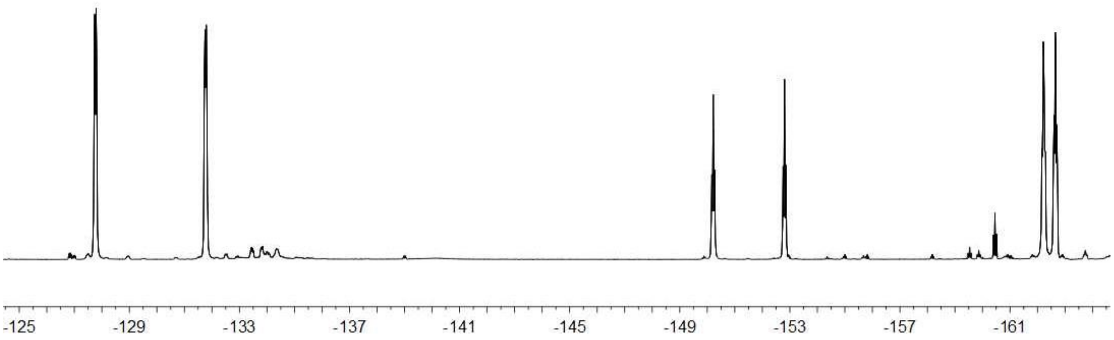


Fig. S9 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299 K, CD_2Cl_2) spectrum of compound **2**.

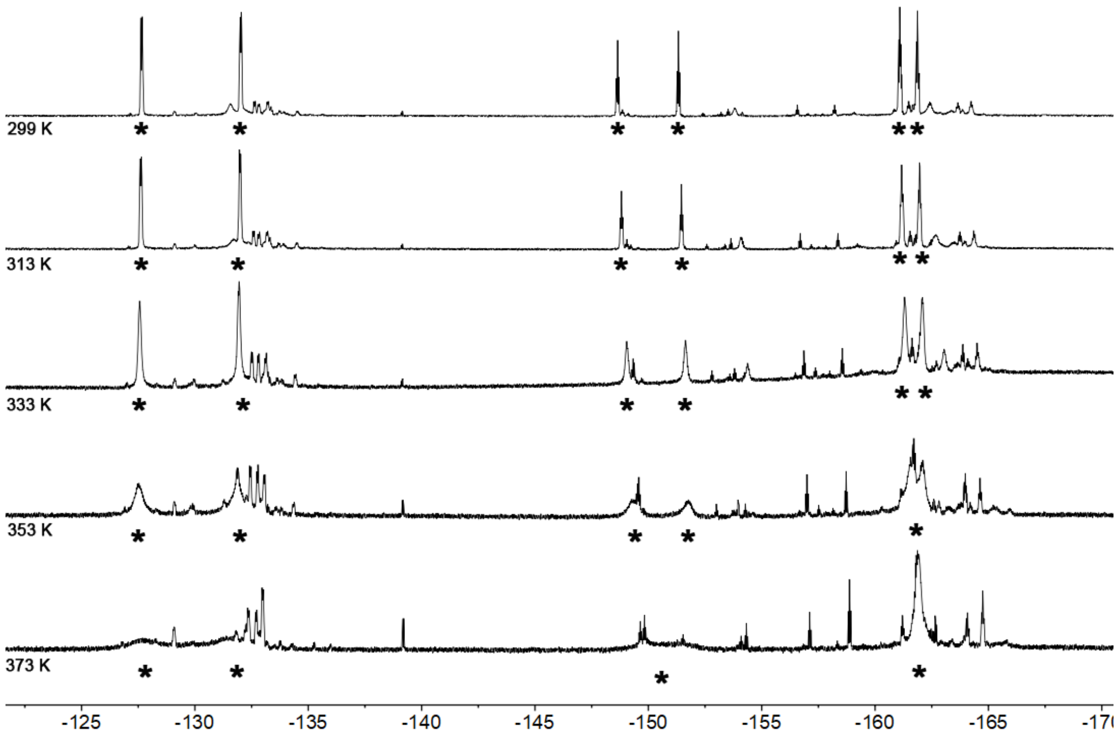
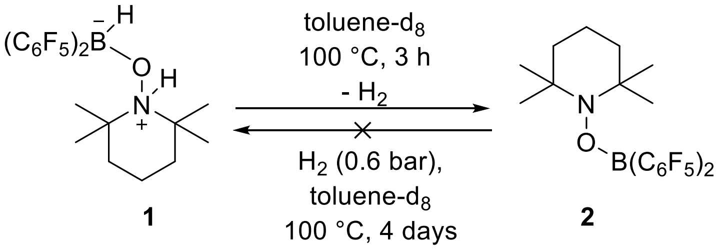


Fig. S10 $^{19}F\{^{1}H\}$ NMR (377 MHz, toluene-d_8) spectra of compound **2** from 299 K to 373 K. [* Compound 2. The rest signals belong to the impurities]

Transformations between compound 1 and compound 2



Scheme S2

(a) **Conversion of compound 1 to 2**: Compound **1** (30.0 mg, 0.06 mmol) was dissolved in toluene-d_8 (1.0 mL) and heated at 100 °C for 50 minutes, then it was characterized by NMR experiments. The NMR data showed that the compound **1** could partly transform into compound **2**. When the reaction time was prolonged to 3 h, compound **1** could transform into compound **2** completely.

(b) **Reaction of compound 2 with H_2**: A solution of compound **2** (19.2 mg, 0.04 mmol) in toluene-d_8 (0.5 mL) was degassed carefully and exposed to H_2 (0.6 bar) at room temperature. After heating at 100 °C for 4 days, it was characterized by NMR experiments. The NMR data showed that compound **2** remained unchanged in this condition.

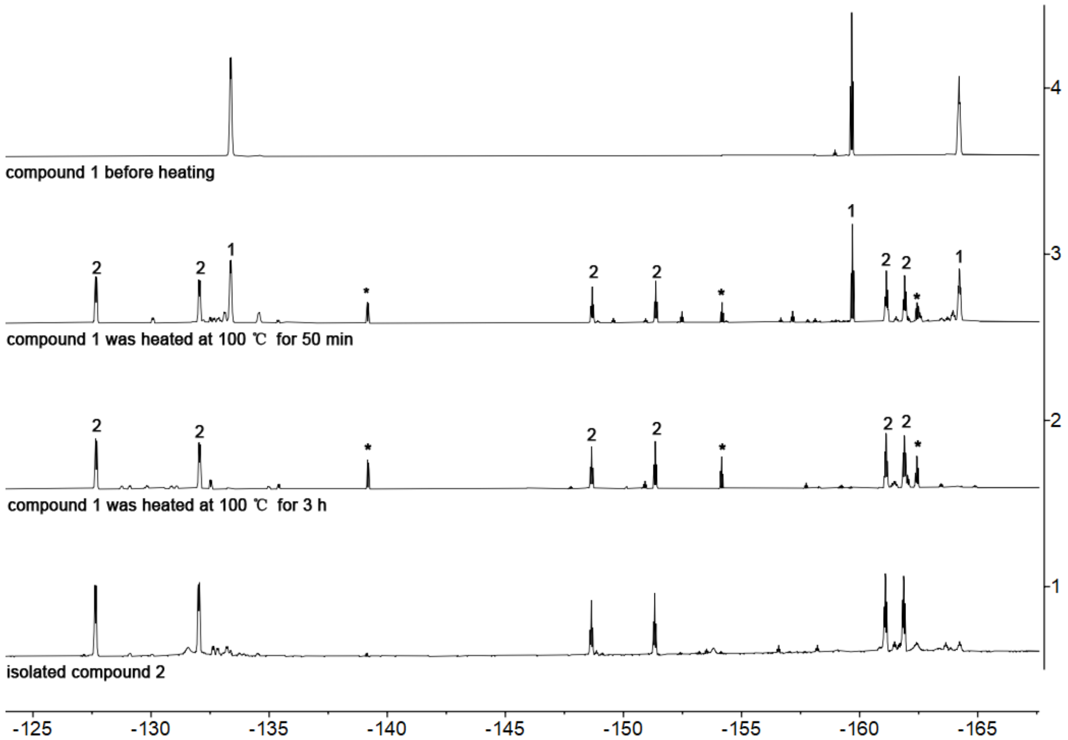
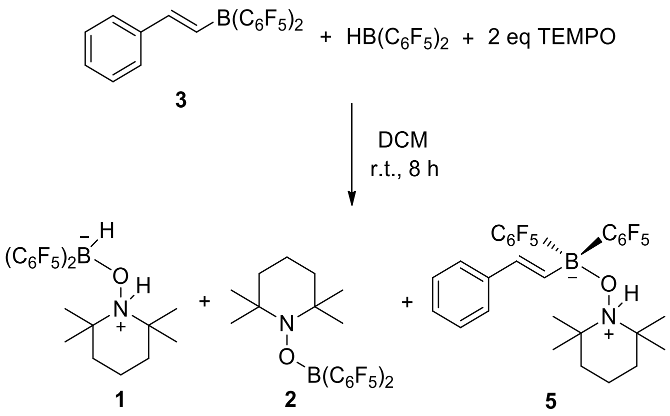


Fig. S11 $^{19}F\{^1H\}$ NMR (377 MHz, 299 K, toluene-d_8) spectra of (1) isolated compound **2** in toluene-d_8, (2) compound **1** was heated in toluene-d_8 at 100 °C for 3 h, (3) compound **1** was heated in toluene-d_8 at 100 °C for 50 min, (4) compound **1** in toluene-d_8 before heating. [* HC_6F_5]

Reactions of TEMPO, alkenylborane 3 and $HB(C_6F_5)_2$



Scheme S3

A solution of alkenylborane **3** (10.0 mg, 0.02 mmol), $HB(C_6F_5)_2$ (7.7 mg, 0.02 mmol) and TEMPO (6.9 mg, 0.04 mmol) in CD_2Cl_2 (0.5 mL) was kept for 8 h at room temperature, then it was characterized by NMR experiments. The NMR data showed that this reaction generated the desired products **2** and **5**, as well as the accidental product **1** and the remaining starting material **3**. The ratio of **2**:**5**:**1**:**3** is 0.57:0.47:0.17:0.09, which is determined by ^{19}F NMR spectroscopy by integration. In the mixture, complex **2** is about 10 mol% more than **5**, coupled with the existence of the product **1** and the remaining starting material **3**, indicating that product **1** was formed from the reaction of $HB(C_6F_5)_2$ and TEMPO.

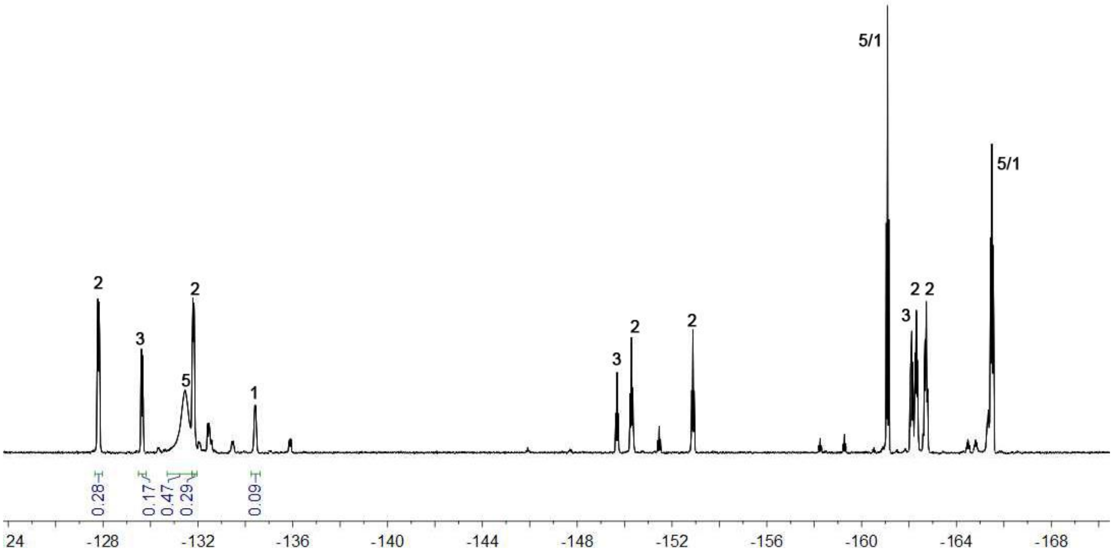


Fig. S12 In-situ $^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2) spectrum of the reaction mixture of **3**, $HB(C_6F_5)_2$ and TEMPO.

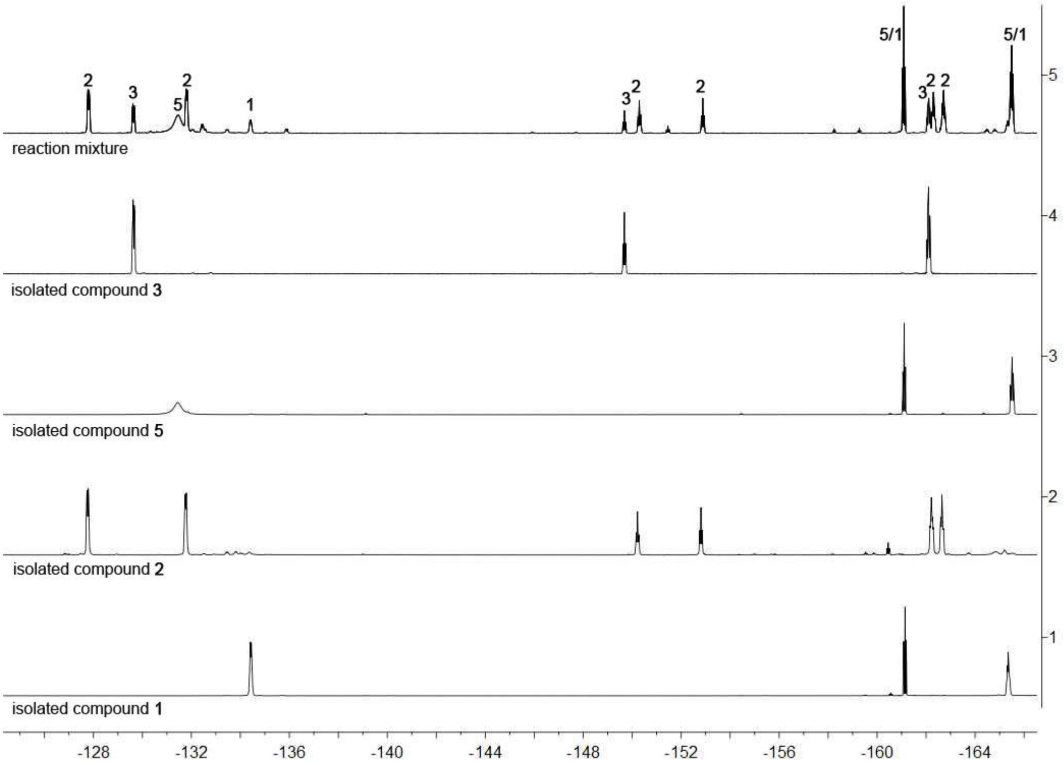


Fig. S13 $^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2) spectra of (1) isolated compound **1**, (2) isolated compound **2**, (3) isolated compound **5**, (4) isolated compound **3**, (5) reaction mixture of **3**, $HB(C_6F_5)_2$ and TEMPO.

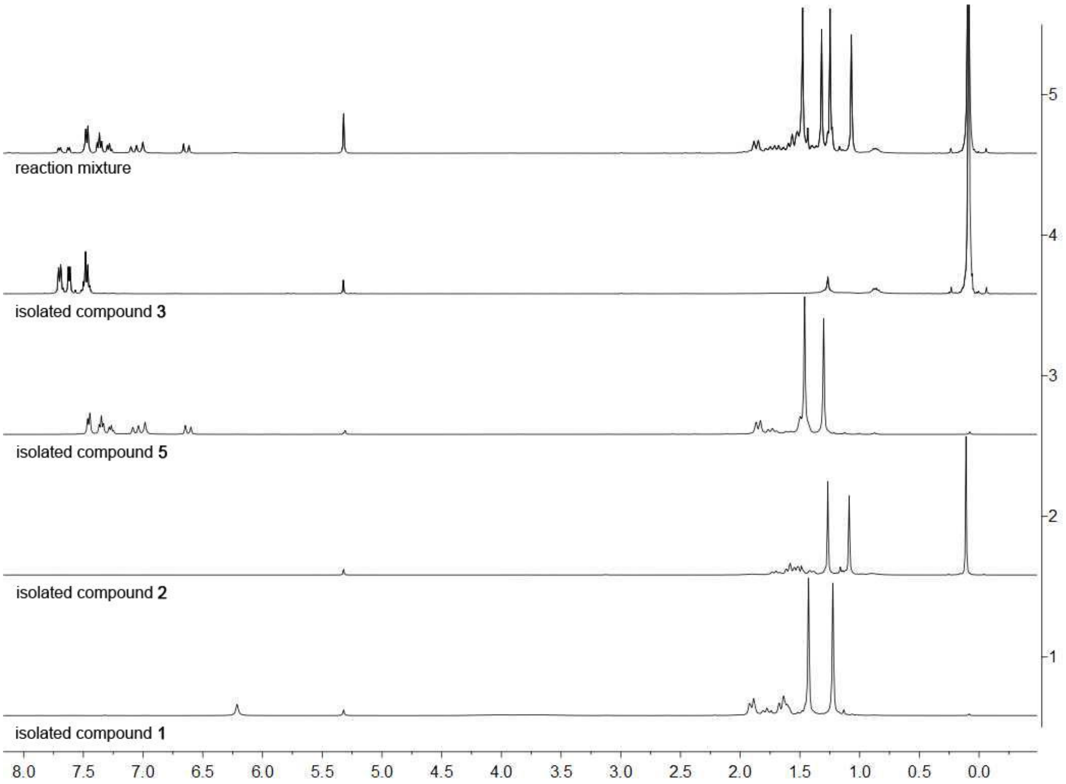


Fig. S14 ^{1}H NMR (400 MHz, 299 K, CD_2Cl_2) spectra of (1) isolated compound **1**, (2) isolated compound **2**, (3) isolated compound **5**, (4) isolated compound **3**, (5) reaction mixture of **3**, $HB(C_6F_5)_2$ and TEMPO.

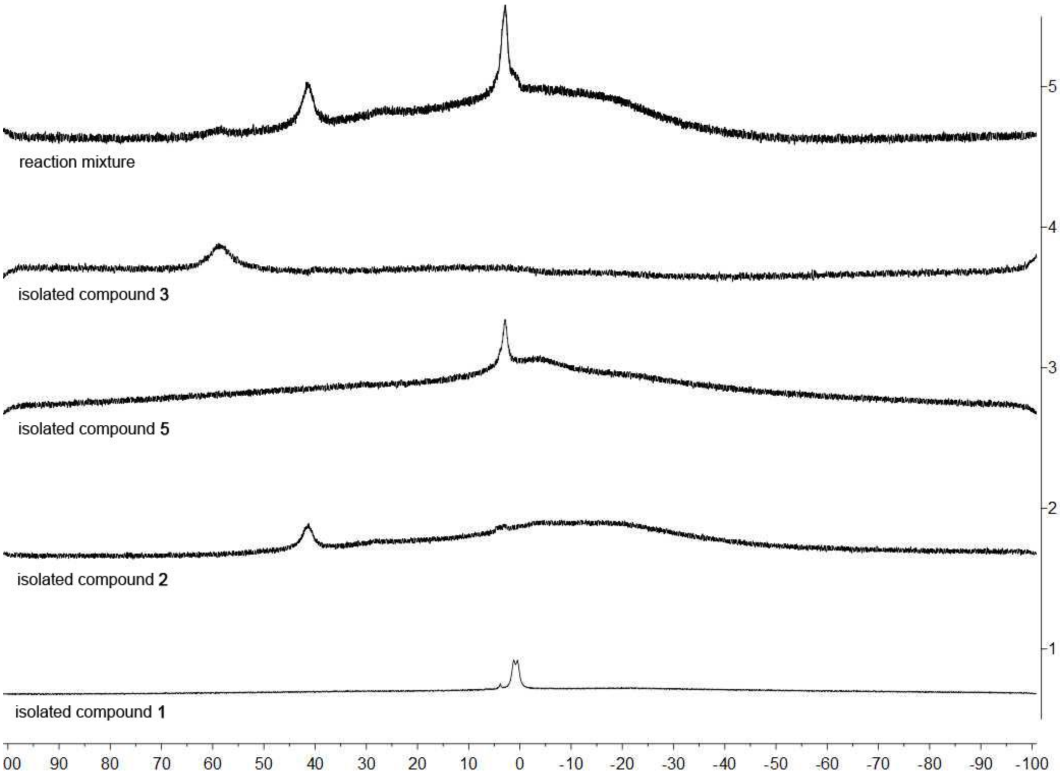
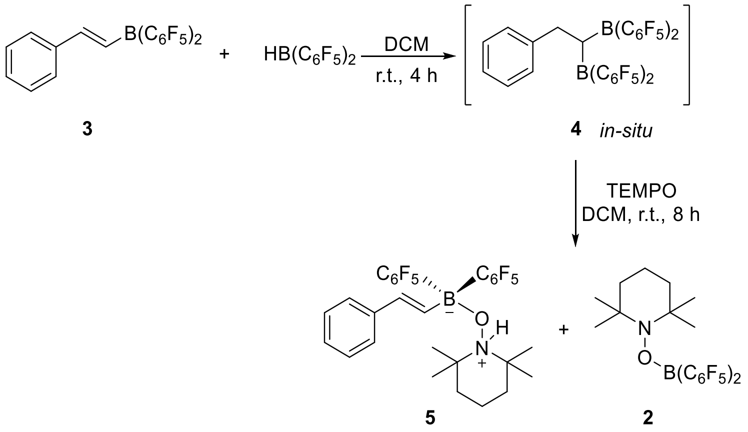


Fig. S15 ^{11}B NMR (128 MHz, 299 K, CD_2Cl_2) spectra of (1) isolated compound **1**, (2) isolated compound **2**, (3) isolated compound **5**, (4) isolated compound **3**, (5) reaction mixture of **3**, $HB(C_6F_5)_2$ and TEMPO.

NMR spectra and crystallographic data of compound 5



Scheme S4

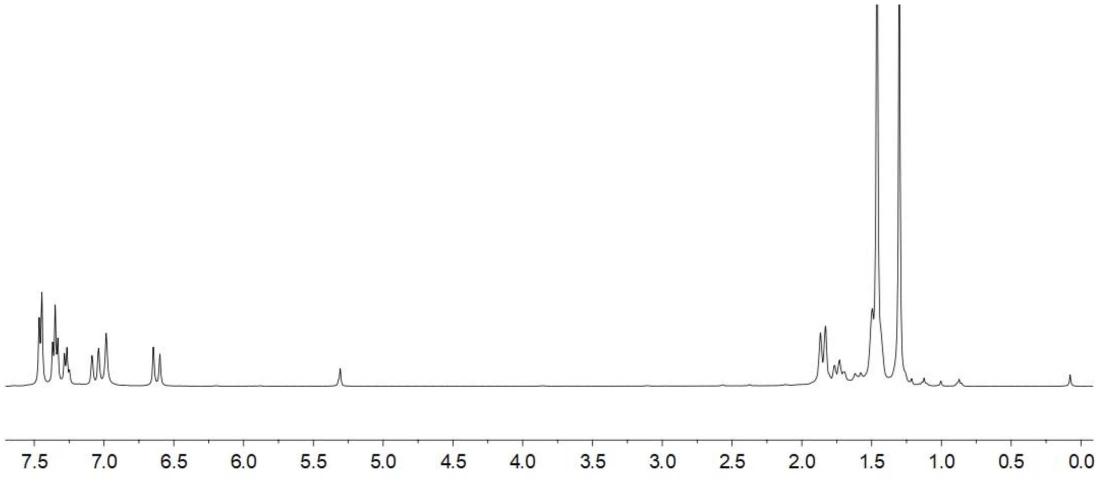


Fig. S16 ^{1}H NMR (400 MHz, 299 K, CD_2Cl_2) spectrum of compound **5**.

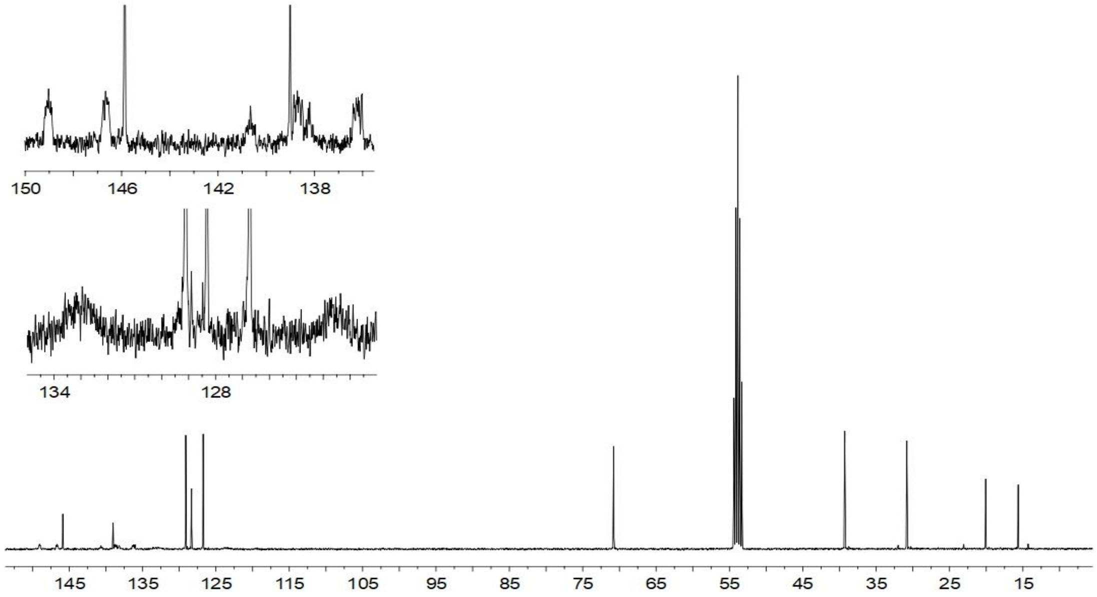


Fig. S17 $^{13}C\{^1H\}$ NMR (101 MHz, 299 K, CD_2Cl_2) spectrum of compound **5**.

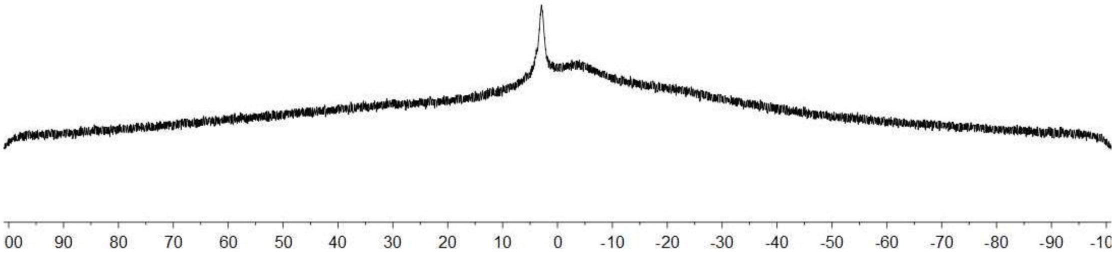


Fig. S18 ^{11}B NMR (128 MHz, 299 K, CD_2Cl_2) spectrum of compound **5**.

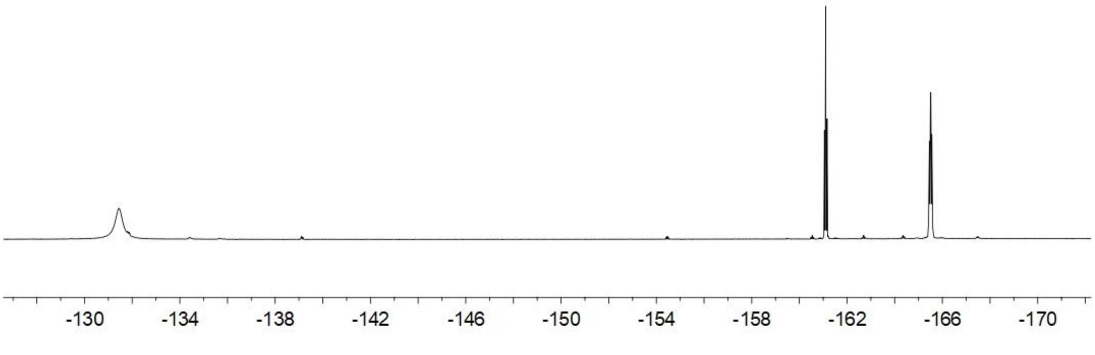


Fig. S19 $^{19}F\{^1H\}$ NMR (377 MHz, 299 K, CD_2Cl_2) spectrum of compound **5**.

X-ray crystal structure analysis of compound 5: formula $C_{29}H_{26}BF_{10}NO$,

M = 605.32, colorless crystal, 0.25 x 0.21 x 0.13 mm, a = 11.8091(8), b = 17.6895(8), c = 16.5586(9) Å, $\alpha = \gamma = 90$, β = 128.367(3)°, V = 2712.1(3) Å^3, ρ_{calc} = 1.482 gcm^{-3}, μ = 0.136 mm^{-1}, empirical absorption correction (0.5955 ≤ T ≤ 0.7456), Z = 4, monoclinic, space group $P2_{1/c}$ (No. 14), λ = 0.71073 Å, T = 200 K, ω and φ scans, 30896 reflections collected (±h, ±k, ±l), 6193 independent (R_{int} = 0.0852) and 3454 observed reflections [I>2σ(I)], 383 refined parameters, R = 0.0519, wR^2 = 0.1196, max. (min.) residual electron density 0.22 (-0.22) e.Å^{-3}, the position of the hydrogen atom at N1 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

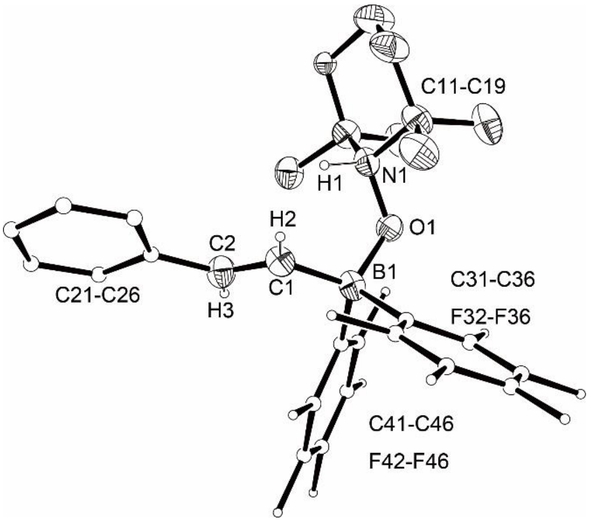
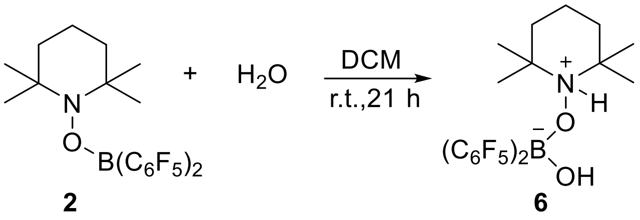


Fig. S20 A view of the molecular structure of compound **5**. (thermal ellipsoids are shown at the 50% probability level). Hydrogen atoms except for N1–H1, C1–H2 and C2–H3 are omitted for clarity.

NMR spectra and crystallographic data of compound 6



Scheme S5

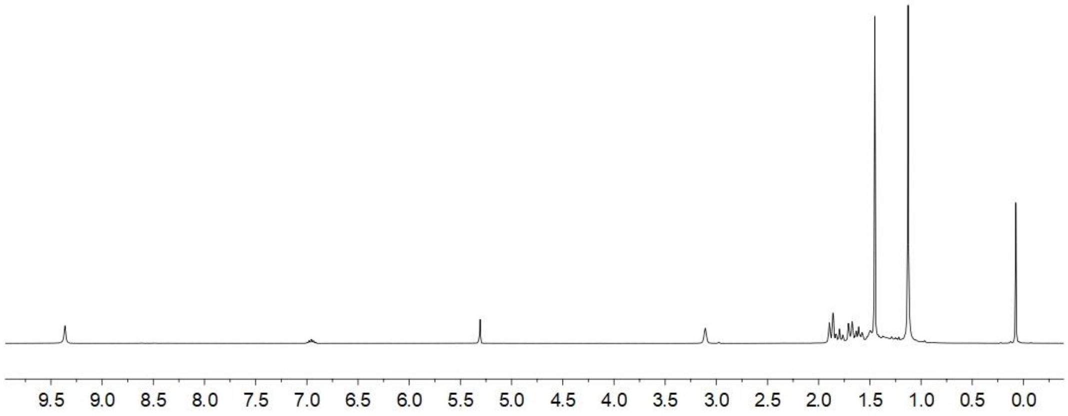


Fig. S21 ^{1}H NMR (400 MHz, 299 K, CD_2Cl_2) spectrum of compound **6**.

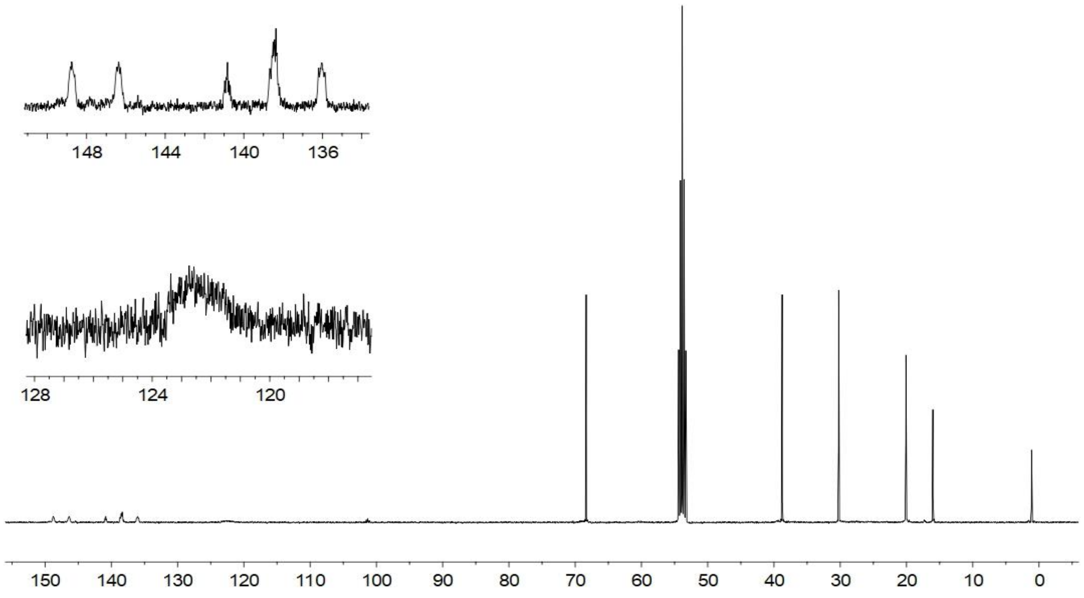


Fig. S22 ^{13}C{^{1}H} NMR (101 MHz, 299 K, CD_2Cl_2) spectrum of compound **6**.

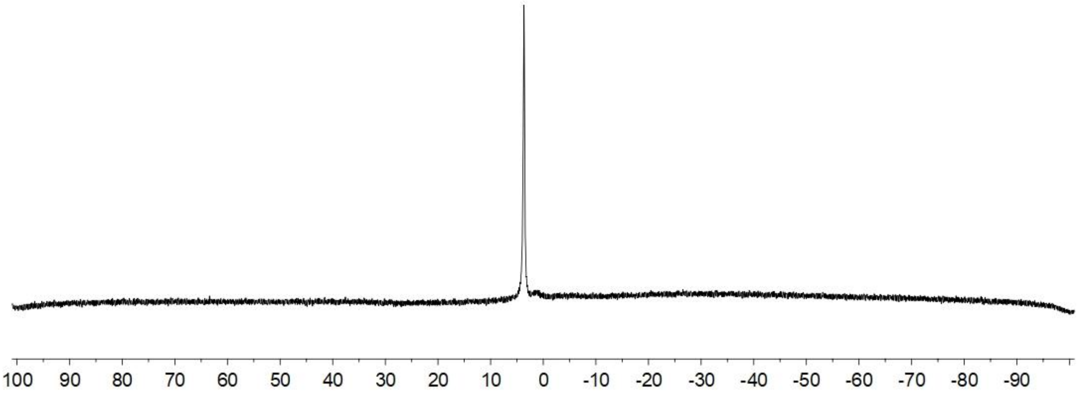


Fig. S23 ^{11}B NMR (128 MHz, 299 K, C_6D_6) spectrum of compound **6**.

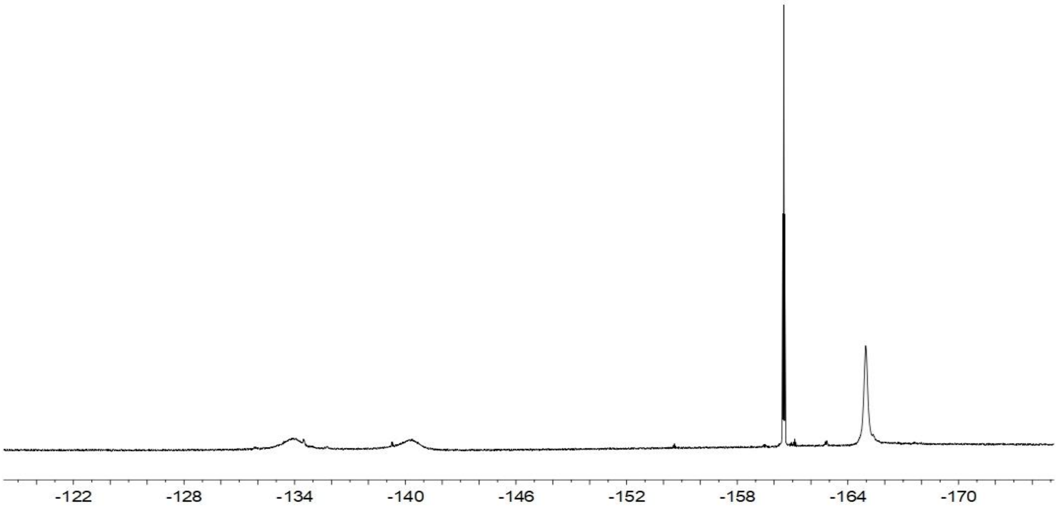


Fig. S24 ^{19}F{^{1}H} NMR (377 MHz, 299 K, C_6D_6) spectrum of compound **6**.

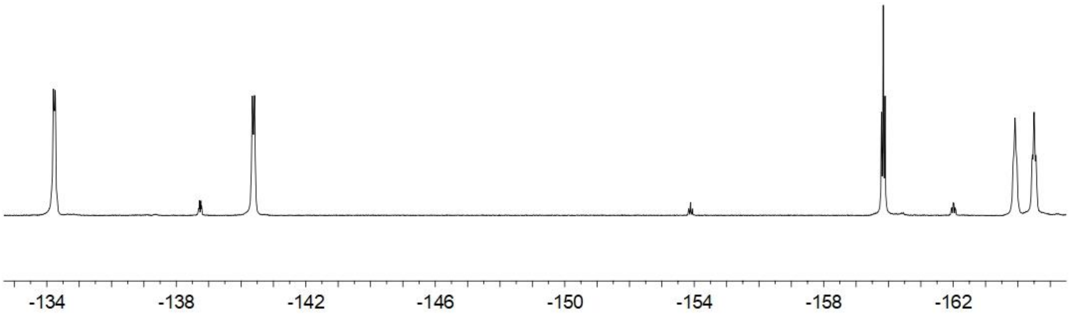


Fig. S25 ^{19}F{^{1}H} NMR (377 MHz, 209 K, CD_2Cl_2) spectrum of compound **6**.

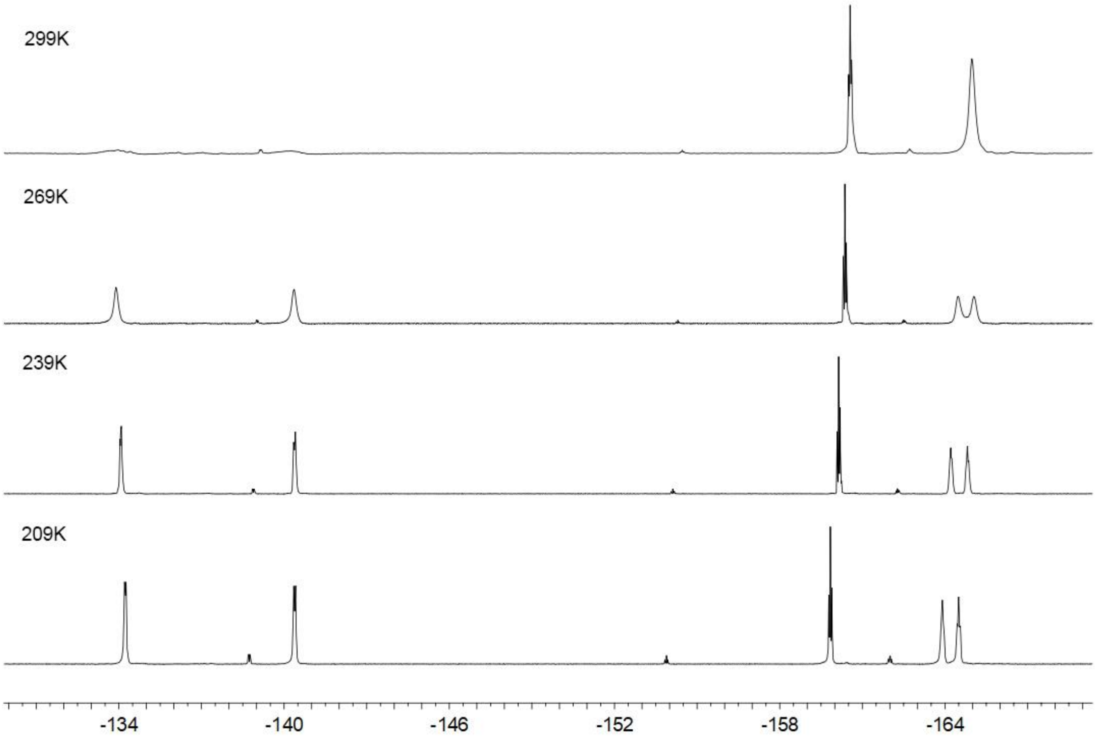


Fig. S26 $^{19}F\{^1H\}$ NMR (377 MHz, CD_2Cl_2) spectra of compound **6** from 299 K to 209 K.

X-ray crystal structure analysis of compound 6: formula $C_{21}H_{20}BF_{10}NO_2$, M = 519.19, colorless crystal, 0.6 x 0.4 x 0.2 mm, a = 9.5625(2), b = 11.9796(3), c = 12.4343(3) Å, α = 66.0090(10), β = 70.1130(10), γ = 56.6920(10)°, V = 1074.76(5) Å^3, ρ_{calc} = 1.604 gcm^{-3}, μ = 0.160 mm^{-1}, empirical absorption correction (0.6679 ≤ T ≤ 0.7465), Z = 2, triclinic, space group P-1 (No. 2), λ = 0.71073 Å, T = 173 K, ω and φ scans, 10926 reflections collected (±h, ±k, ±l), 6579 independent (R_{int} = 0.0168) and 5458 observed reflections [$I>2\sigma(I)$], 324 refined parameters, R = 0.0382, wR^2 = 0.1115, max. (min.) residual electron density 0.452 (-0.321) e.Å^{-3}, the positions of the hydrogen atom at O2 and N1 were refined freely;

others hydrogen atoms were calculated and refined as riding atoms.

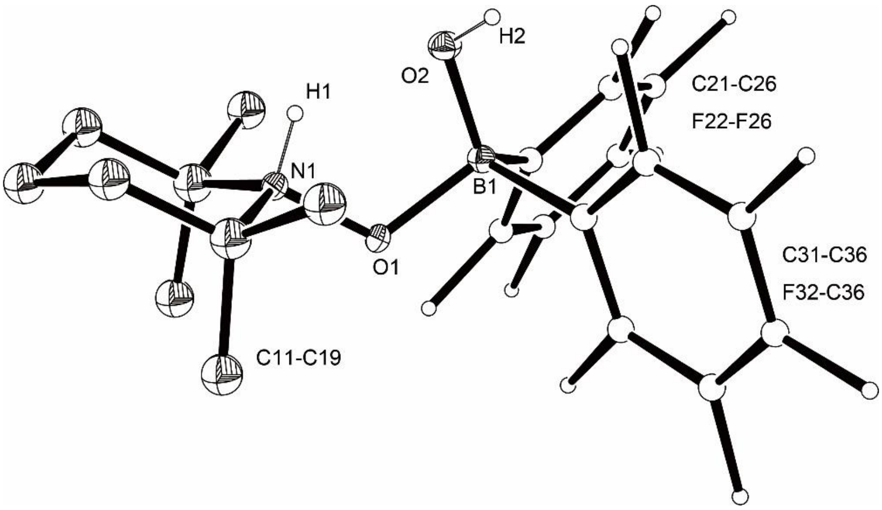
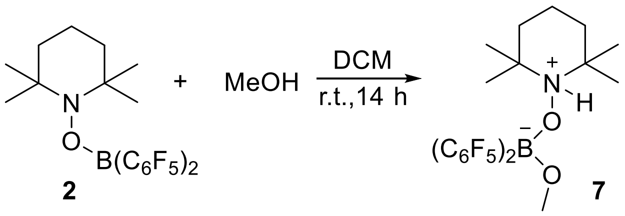


Fig. S27 Molecular structure of compound **6** (thermal ellipsoids are shown at the 50% probability level). Hydrogen atoms except for N1–H1 and O2–H2 are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-O1 1.413(1), B1-O1 1.543(2), B1-O2 1.452(1); B1-O1-N1 114.84(7), $\sum \mathrm{N1}^{\mathrm{CCO}}$ 338.81, $\sum \mathrm{B1}^{\mathrm{C21C31O1}}$ 322.21.

NMR spectra and crystallographic data of compound 7



Scheme S6

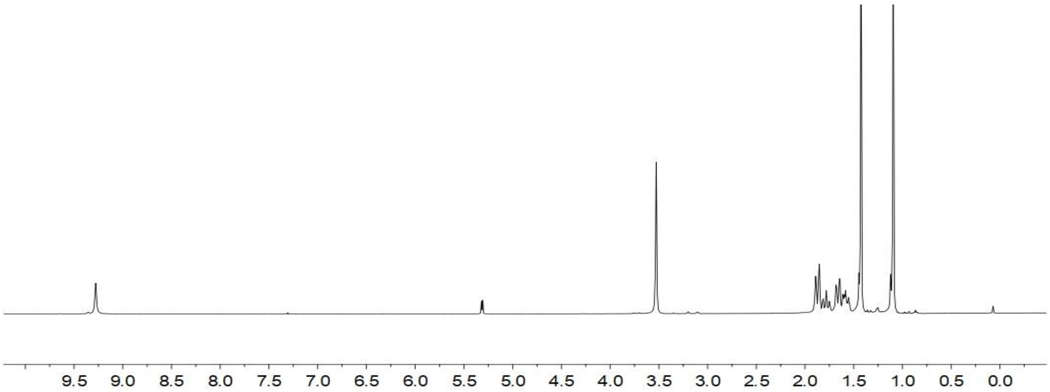


Fig. S28 ^{1}H NMR (400 MHz, 299 K, CD_2Cl_2) spectrum of compound **7**.

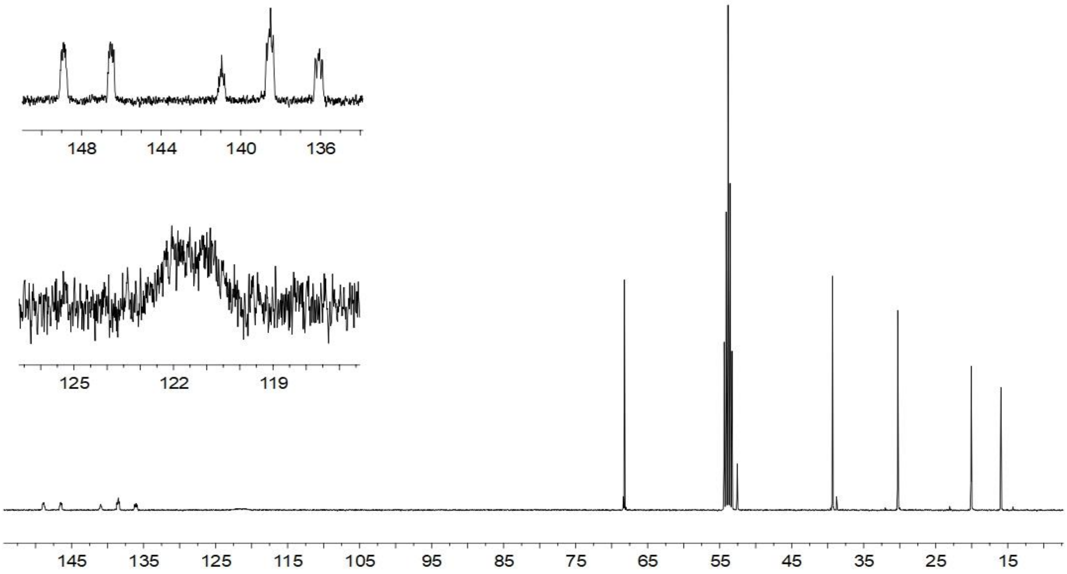


Fig. S29 $^{13}C\{^{1}H\}$ NMR (101 MHz, 299 K, CD_2Cl_2) spectrum of compound **7**.

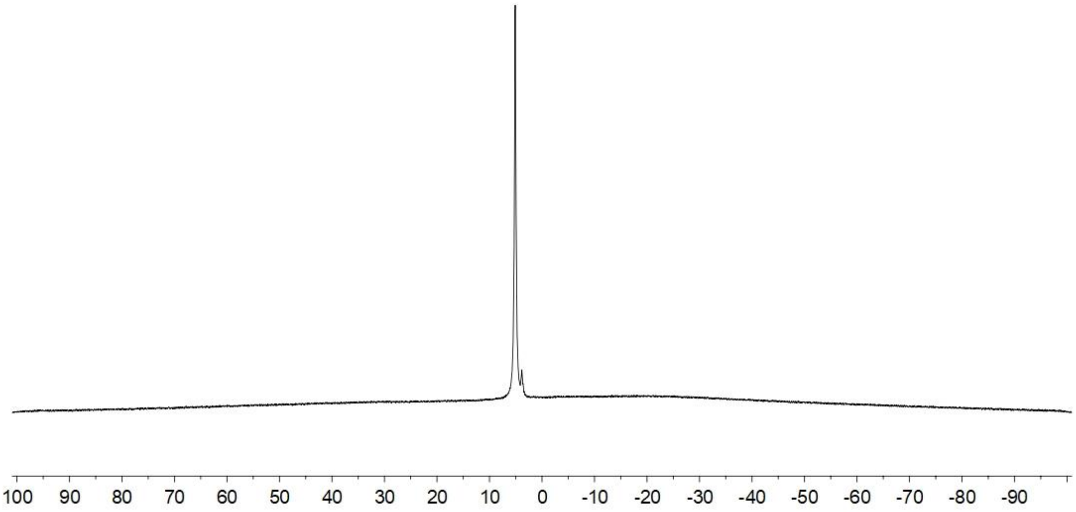


Fig. S30 ^{11}B NMR (128 MHz, 299 K, CD_2Cl_2) spectrum of compound **7**.

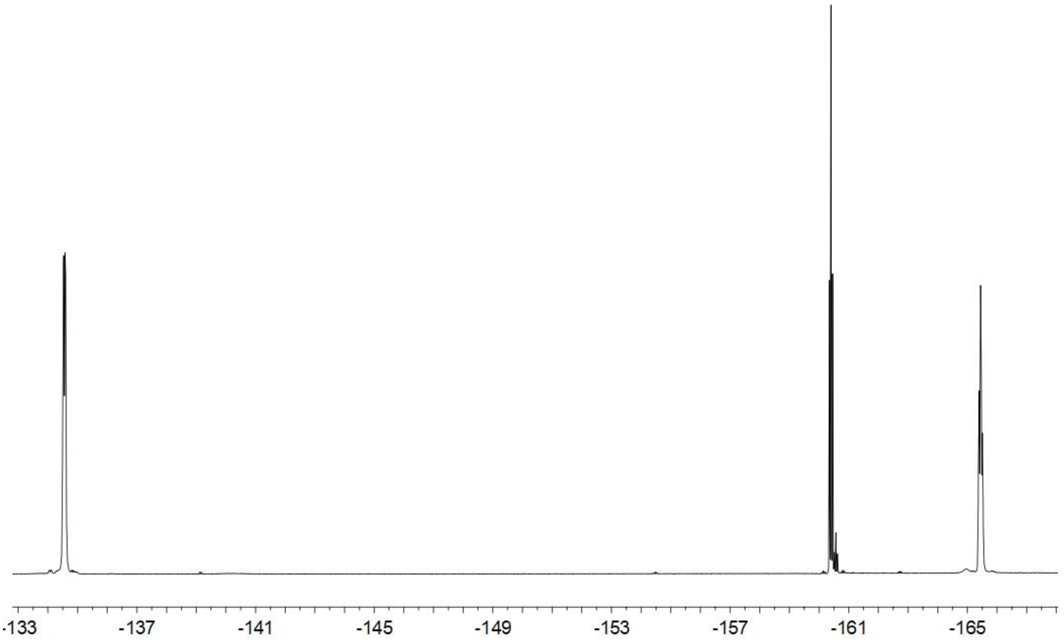


Fig. S31 ^{19}F{^{1}H} NMR (377 MHz, 299 K, CD_2Cl_2) spectrum of compound **7**.

X-ray crystal structure analysis of compound 7: formula $C_{22}H_{22}BF_{10}NO_2$, M = 533.21, colorless crystal, 0.6 x 0.43 x 0.26 mm, a = 10.4834(2), b = 11.7933(3), c = 11.9729(3) Å, α = 114.2010(10), β =

95.4820(10), γ = 110.8550(10)°, V = 1210.01(5) Å^3, ρ_{calc} = 1.463 gcm^{-3}, μ = 0.144 mm^{-1}, empirical absorption correction (0.6750 ≤ T ≤ 0.7463), Z = 2, triclinic, space group P-1 (No. 2), λ = 0.71073 Å, T = 173 K, ω and φ scans, 11307 reflections collected (±h, ±k, ±l), 6343 independent (R_{int} = 0.0182) and 5340 observed reflections [I>2σ(I)], 334 refined parameters, R = 0.0368, wR^2 = 0.1097, max. (min.) residual electron density 0.46 (-0.28) e.Å^{-3}, the position of the hydrogen atom at N1 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

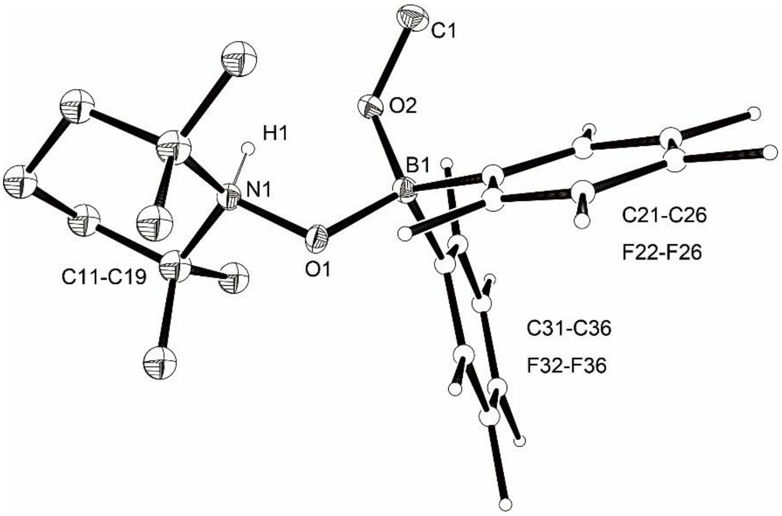
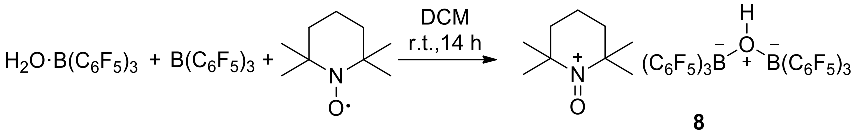


Fig. S32 A view of the molecular structure of compound **7**. (thermal ellipsoids are shown at the 50% probability level). Hydrogen atoms except for N1–H1 are omitted for clarity.

NMR spectra and crystallographic data of compound 8



Scheme S7

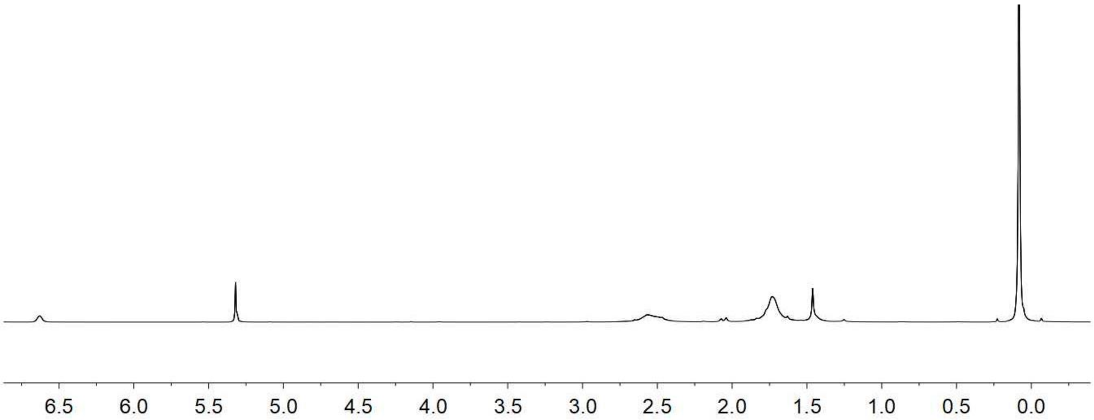


Fig. S33 ^{1}H NMR (400 MHz, 299 K, CD_2Cl_2) spectrum of compound **8**.

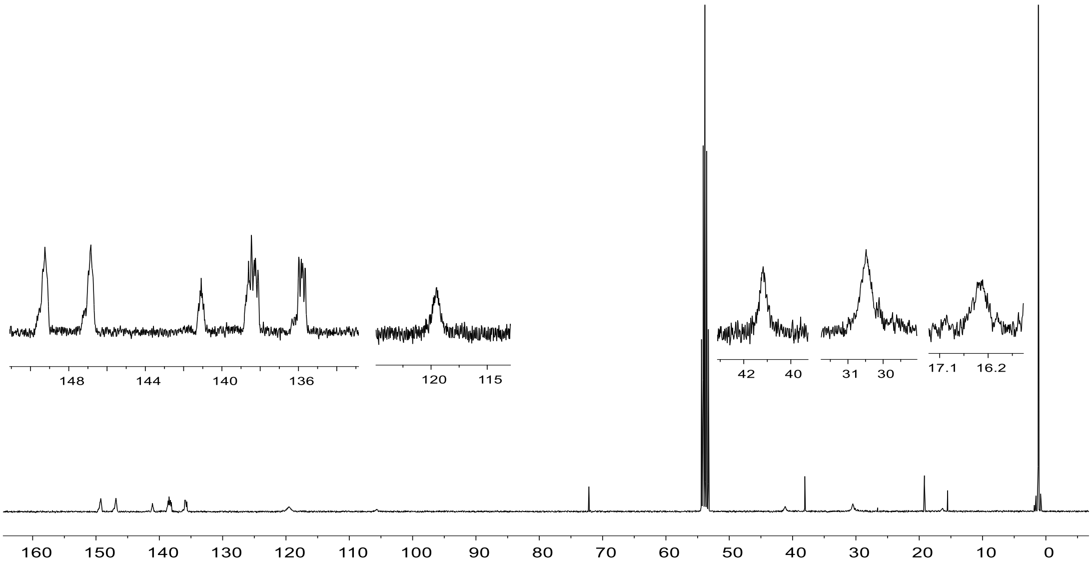


Fig. S34 ^{13}C{^{1}H} NMR (101 MHz, 299 K, CD_2Cl_2) spectrum of compound **8**.

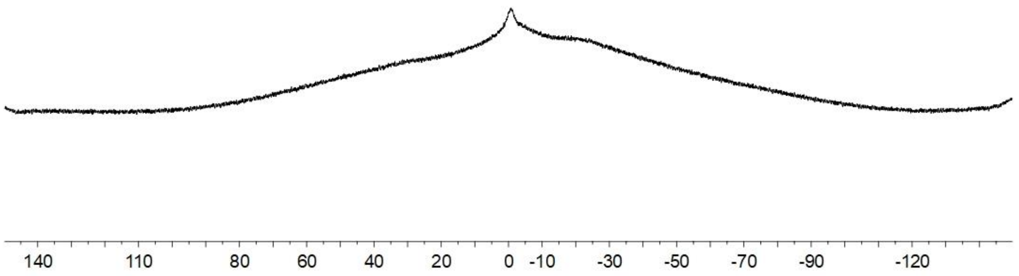


Fig. S35 ^{11}B NMR (128 MHz, 299 K, C_6D_6) spectrum of compound **8**.

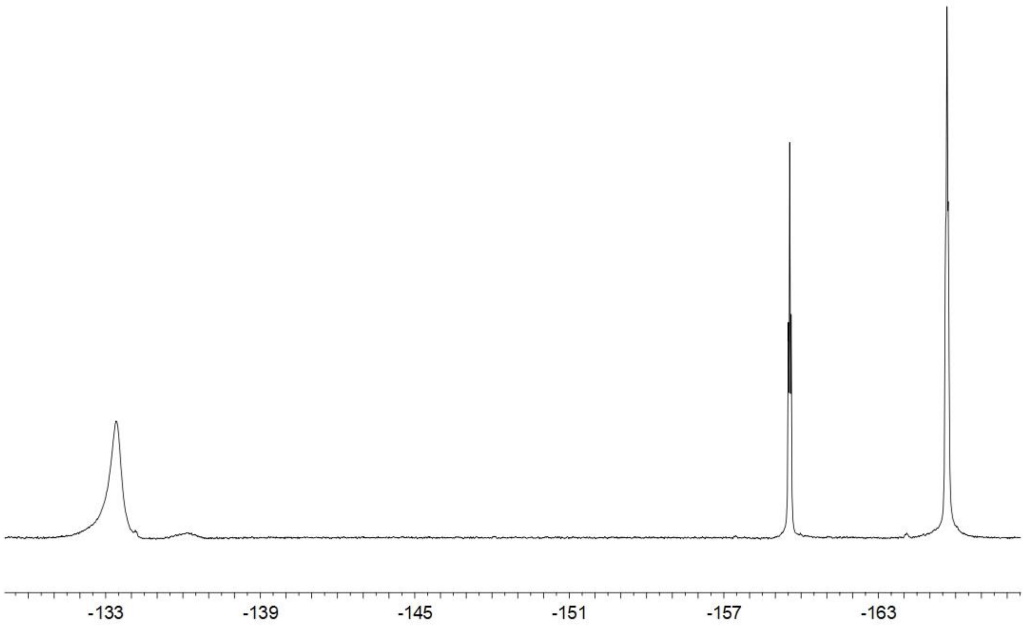


Fig. S36 ^{19}F{^{1}H} NMR (377 MHz, 299 K, C_6D_6) spectrum of compound **8**.

X-ray crystal structure analysis of compound 8: formula $C_{46}H_{21}Cl_2B_2F_{30}NO_2$, M = 1282.16, yellow crystal, 0.6 x 0.4 x 0.2 mm, a = 11.994(4), b = 13.023 (4), c = 17.033(5) Å, α = 81.550(10), β = 85.189(9), γ = 69.211(9)°, V = 2458.9(13) Å^3, ρ_{calc} = 1.732 gcm^{-3}, μ = 0.288 mm^{-1}, empirical absorption correction (0.919 ≤ T ≤ 0.965), Z = 2, triclinic, space group P-1 (No. 2), λ = 0.71073 Å, T = 173 K, ω and φ scans, 47929 reflections collected (±*h*, ±*k*, ±*l*), 8634 independent (R_{int} = 0.1271) and 4677 observed reflections [I>2σ(I)], 729 refined parameters, R = 0.0760, wR^2 = 0.1947, max. (min.) residual electron density 0.473 (-0.436) e.Å^{-3}, the position of the hydrogen atom at O1 as refined freely; others hydrogen atoms were calculated and refined as riding atoms.

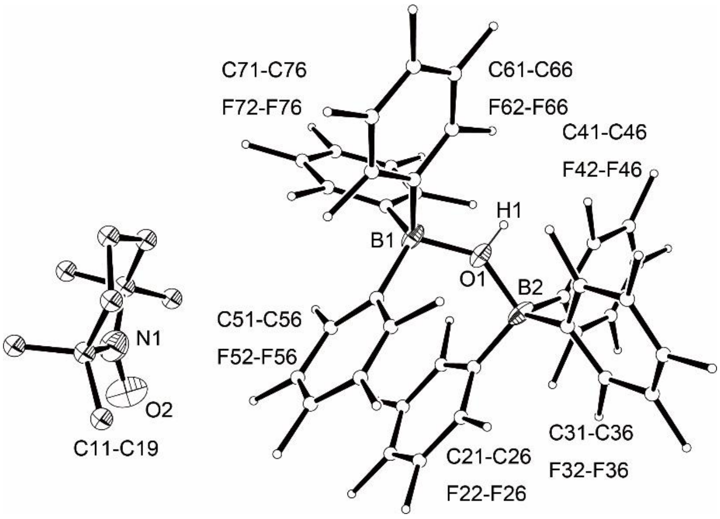
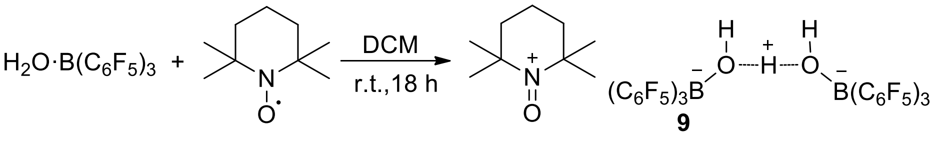


Fig. S37 Molecular structure of compound **8** (thermal ellipsoids are shown at the 50% probability level). Hydrogen atoms except for O1–H1 are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-O2 1.226(6), B1-O1 1.565(6), B2-O1 1.576(5); B1-O1-B2 141.5(4), $\sum N1^{CCO}$ 359.9, $\sum B1^{CCC}$ 332.9, $\sum B2^{CCC}$ 334.3.

NMR spectra and crystallographic data of compound 9



Scheme S8

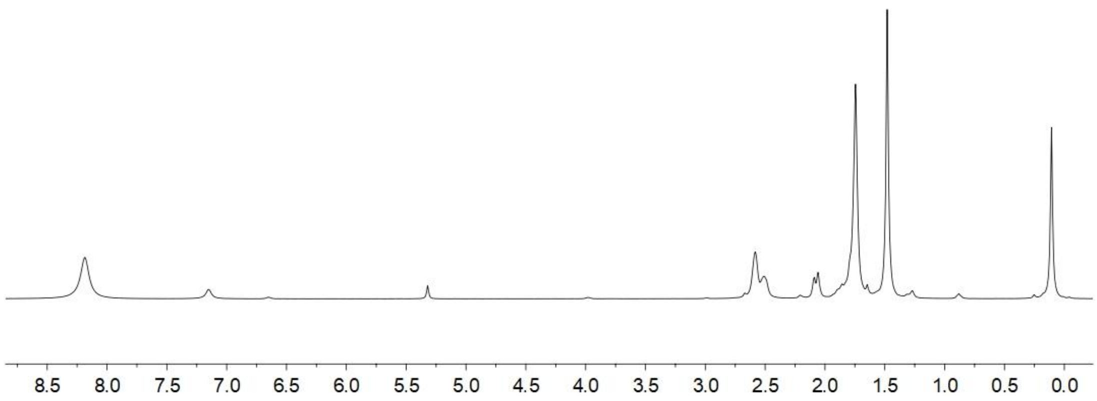


Fig. S38 ^{1}H NMR (400 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**.

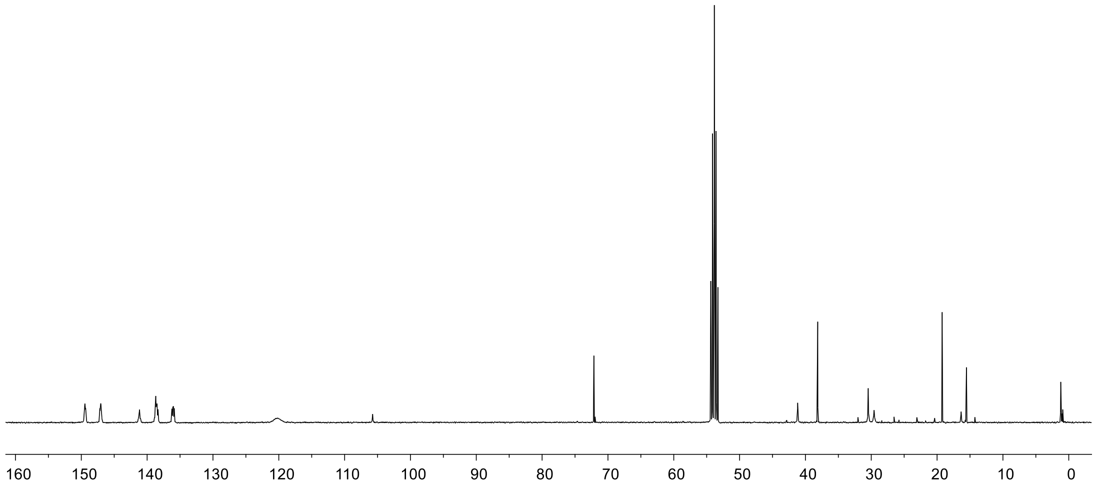


Fig. S39 ^{13}C{^{1}H} NMR (101 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**.

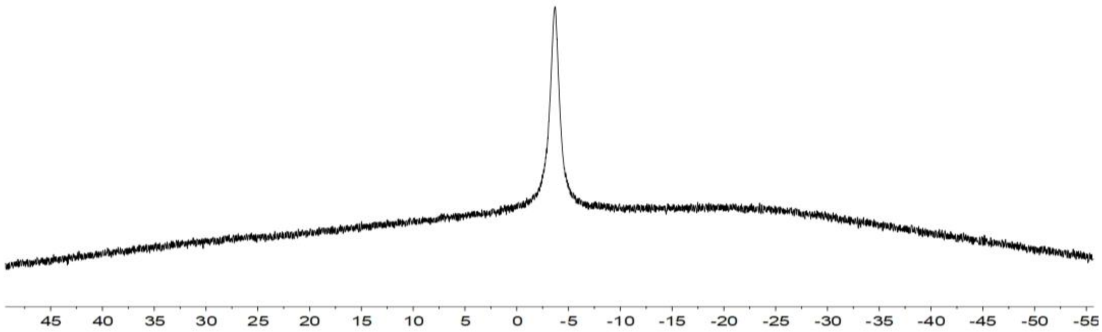


Fig. S40 ^{11}B NMR (128 MHz, 299 K, C_6D_6) spectrum of compound **9**.

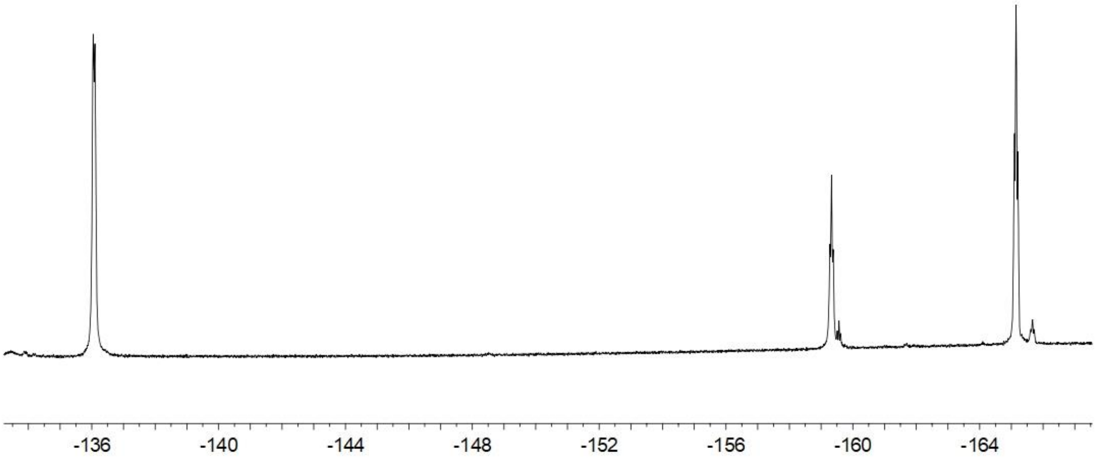


Fig. S41 $^{19}F\{^{1}H\}$ NMR (377 MHz, 299 K, C_6D_6) spectrum of compound **9**.

X-ray crystal structure analysis of compound 9: formula $C_{45}H_{21}B_2F_{30}NO_3$, M = 1215.25, yellow crystal, 0.3 x 0.2 x 0.2 mm, a = 12.5804(11), b = 13.3091(12), c = 16.1032(16) Å, α = 67.740(3), β = 69.334(3), γ = 79.055(3)°, V = 2329.8(4) Å^3, ρ_{calc} = 1.732 gcm^{-3}, μ = 0.189 mm^{-1}, empirical absorption correction ($0.6905 \leq T \leq 0.7456$), Z = 2, triclinic, space group P-1 (No. 2), λ = 0.71073 Å, T = 200 K, ω and φ scans, 54129 reflections collected ($\pm h$, $\pm k$, $\pm l$), 10732 independent (R_{int} = 0.0405) and 8164 observed reflections [$I > 2\sigma(I)$], 746 refined parameters, R = 0.0371, wR^2 = 0.0921, max. (min.) residual electron density 0.28 (-0.25) e.Å^{-3}, the positions of the hydrogen atom at O1 and O2 were refined freely; others hydrogen atoms were calculated and refined as riding atoms.

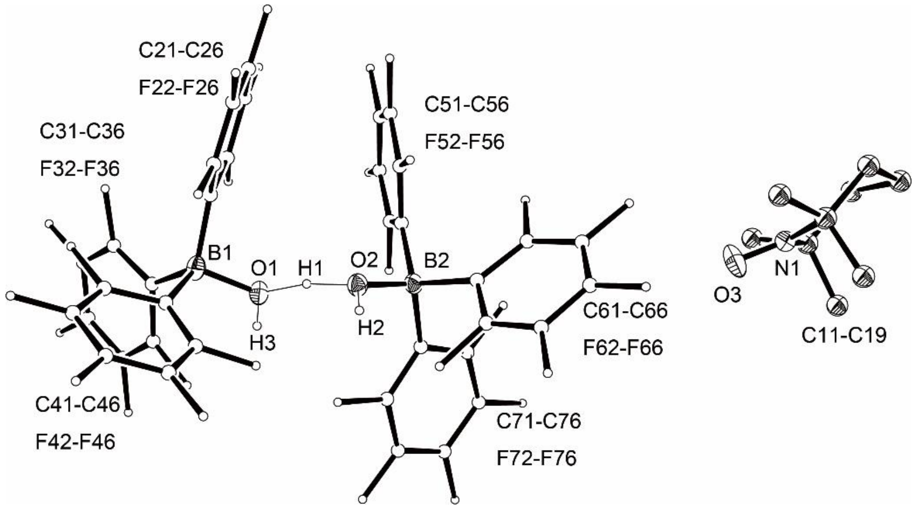


Fig. S42 Molecular structure of compound **9** (thermal ellipsoids are shown at the 50% probability level). Hydrogen atoms except for O–H are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-O3 1.188(2), B1-O1 1.520(2), B2-O2 1.522(2), O1-H1 1.18(3), O1-H3 0.81(2), O2-H1 1.25(3), O2-H2 0.82(2); $\sum$N1^{CCO} 359.9, $\sum$B1^{CCC} 336.0, $\sum$B2^{CCC} 333.9.

The evidence of H_2 product in the reaction of TEMPO and $H_2O{\cdot}B(C_6F_5)_3$

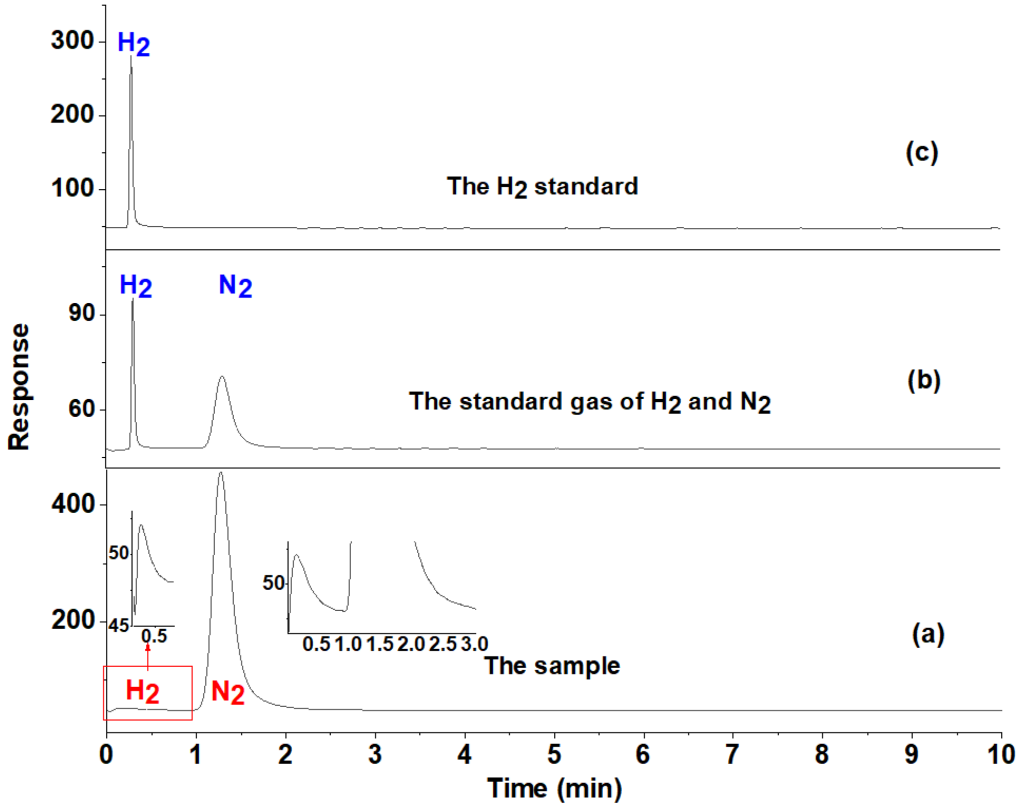


Figure S43. GC chromatograms from a thermal conductivity detector (TCD) of (a) the sample, (b) the standard gas of H_2 and N_2, (c) the standard gas of H_2. Carrier gas: argon. The gas product was sampled from the atmosphere in a NMR tube, which involves a mixture of $H_2O{\cdot}B(C_6F_5)_3$ (150.0 mg, 0.28 mmol) and TEMPO (22.1 mg, 0.14 mmol) in 0.5 mL DCM under N_2 atmosphere.